EXPERIMENTAL DEVELOPMENT OF A TECHNIQUE FOR THE CORRELATION OF FLIGHT- AND GROUND-BASED STUDIES OF THE ULTRAVIOLET DEGRADATION OF POLYMER FILMS

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SUMMARY

The surface temperatures and the environmental stabilities of thermal control surfaces have been observed to change measurably in a near-earth orbit on the S-16 Orbiting Solar Observatory (OSO). The changes in surface temperatures caused by in-space ultraviolet degradation do not correlate with predictions from ground-based simulation of environmental conditions. The general behavior of these surfaces has suggested a possible technique of evaluating the accuracy of ground-based simulation experiments, namely, the measurement of surface temperature of a film consisting of a well-behaved polymer system. Films of both polymers and copolymers of vinyl chloride were exposed to ultraviolet radiation in vacuum and were found to exhibit a regular and quantitatively measurable change in solar absorptance with time. The major changes produced by this exposure occurred in the ultraviolet and visible regions. Virtually no change has been observed in the infrared absorption spectra of these films, even after exposure to the equivalent of 72 hours of space solar radiation. In the exposures to simulated conditions of vacuum and ultraviolet radiation, a linear change with time in the ratio of solar absorptance to emittance has been observed to occur after an initial transient period. The regular behavior of these films indicates that a reasonable prediction of the temperature changes which would occur in the real space environment can be made.

To obtain the desired mechanical properties for a flight test, a surface consisting of a pure polyvinyl chloride terpolymer film (VMCH) was cast on a polished aluminum substrate. This material is found experimentally to behave almost identically to the pure polyvinyl chloride. Predicted temperature changes of such a surface will be compared with the actual results obtained by orbiting the surface on the S-57 OSO. The amount of gamma radiation required to produce a given change in the absorptance equivalent to that produced by a specific amount of ultraviolet radiation has also been determined experimentally. The gamma radiation which would produce the same effect as

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a 9-hour exposure to the solar ultraviolet would require a period of 3 or 4 years exposure in space; and, hence, would not influence the results of the correlation of the ultraviolet exposure. AUTHOR

INTRODUCTION

Reflective white paints, consisting of inorganic pigments and organic polymeric binders, have been employed as thermal control surfaces for space vehicles. A variety of polymeric types of binders have been investigated for this purpose. Paints based on acrylics, silicones, phenolics, and epoxy resins have been used (ref. 1). None of these materials are unstable in a vacuum in the range of operating temperatures encountered on a spacecraft. The inorganic pigments, for example, titanium dioxide, are relatively stable to the action of the incident electromagnetic radiation encountered in these applications. All available evidence obtained to date points to an alteration of the molecular structure of the polymeric components produced by the incident ultraviolet radiation as the principal cause of change in the thermal control characteristics of these coatings. Nine percent of the total energy of incident solar radiation in near-earth orbit lies in the region from 2200 to 4000 Å and only 0.02 percent below 2200 Å (ref. 2). The energy of photons in the wave-length region from 2200 to 4000 Å ranges from 5.6 to 3.1 electron volts. These photons have sufficient energy to break carbon-carbon bonds characteristic of organic polymers, the strength of which is of the order of 3 electron volts (72 kcal per mole), and this can initiate molecular damage processes. The specific chemical structure of the polymeric binder determines both the specific wave lengths and the degree of absorption of the incident ultraviolet radiation. The basic chemical constitution of the polymer also determines the course of the ensuing degradation reaction.

The degradation reaction may produce scissions, cross-linking, or functional group alteration. Only when the damage process leads to the production of highly absorbing groups may one expect a significant change in the optical properties of coatings formulated from these polymers.

To correlate quantitatively the effects of a simulated environment with those of an actual orbital flight on the rate of change of temperature of a polymeric film, a basic polymer with the following properties is required:

(1) It absorbs photons in the range from 2200 to at least 3000 Å and these photons should be effective in generating color-producing groups.

(2) Its principal damage reaction is chromophore production so that absorptivity changes in a regular manner with time of exposure. (Under the conditions of exposure there should be no significant autocatalysis; that is, this reaction should be zero order with respect to the chromophoric reaction.)

(3) It undergoes the required chromophoric reaction without significant alteration in the basic mechanical properties of the film; that is, its physical properties should not be affected either by cross-linking or by scission so that the film can endure a reasonable orbital flight and experience the expected temperature changes while still retaining its mechanical integrity.

(4) Its specific color-producing reactions are free from the the effects of differences in spectral distribution. The quantum efficiency and both the number and kinds of groups formed should be independent of the wave length of ultra-violet radiation absorbed.

(5) It is sufficiently stable at the operating temperature of the film that thermal degradation does not occur, and thus complicate the interpretation of the ultraviolet damage process.

Information on the photochemical degradation reactions of polyvinyl chloride and copolymers containing a substantial portion of polyvinyl chloride monomer suggests that such polymers could possibly meet the foregoing requirements (ref. 3).

The specific research to be described is concerned with the evaluation of thin films of polymers and copolymers of vinyl chloride as indicator coatings, as well as with approaches to ground-based simulation which, if successful, could be used ultimately to predict both the expected temperatures and temperature changes with time of exposure to solar radiation. This paper discusses the research to date on the ground-based phase of this program. The results obtained herein will be correlated ultimately with an in-flight test on the S-57 Orbiting Solar Observatory which should provide an evaulation of the simulation technique.

EXPERIMENTAL RESULTS

TiO_2-Epoxy and TiO_2-Silicone Coatings Used as Thermal Control Surfaces on the S-16 OSO Satellite

The surface temperatures attained by TiO_2-epoxy and TiO_2-silicone coatings during the first orbit of the S-16 OSO are shown in figure 1. It can be seen that the maximum temperature reached by the TiO_2-epoxy

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coating is about 15° F, whereas that of the TiO_2-silicone coating is about 30° F. These temperatures agree with those calculated by the relation given in reference 3 with initial values for α_S/ϵ for these coatings of 0.27 and 0.36.

The increase in solar absorptance of these coatings calculated from the observed increases in surface temperature in the space environment is shown in figure 2. Here the increase in solar absorptance is given as a function of exposure in equivalent sun hours in a near-earth orbit. A nonlinear change in solar absorptance with time indicates the presence of an autocatalytic effect. At the beginning of the exposure, the rate of change in the epoxy is greater than in the silicone coating, but after 10^3 equivalent sun hours, the rate of change of the silicone solar absorptance is essentially the same as that for the epoxy coating. These differences in environmental aging characteristics are apparently due to basic differences in the photochemistry of the two polymer binders concerned.

These specific changes in the solar absorptance obtained from in-flight measurements of the temperature have been compared with the changes predicted by ground-based simulation experiments by two different groups of investigators. Unfortunately, the ground-based experiments cannot perfectly reproduce the conditions of space. Specifically, the temperature of the films during ultraviolet irradiation and the intensity and spectral distribution match of the simulation lamps were not the same as the space exposure in any of these experiments. In the test run with a BH-6 lamp, the average film temperature was 185° F at 7 solar constants of ultraviolet flux. With an AH-6 lamp, on the other hand, the temperature was 75° F with 1 to 10 solar constants. The results are compared in figures 3 and 4 with the flight results with an average in-flight temperature of 0° F at one solar constant. For the time interval of exposure considered, there is apparently better agreement between the actual and the predicted values of absorptance change with the flight test in the case of the silicone (fig. 4) than in the case of the epoxy (fig. 3). The tests suggest that the rate of change of solar absorptance is dependent on changes in the aforementioned test parameters for the polymeric systems in question. These results cannot be interpreted more precisely until the relationships among the rate of chromophore production, temperature, intensity, and wave length are established.

Some of the difficulties involved in obtaining a simulation match between an ultraviolet mercury vapor lamp and the actual solar radiation are shown in figure 5. In this particular case, the distance from the lamp source to the detector (or sample) has been adjusted to provide an average of one solar constant of ultraviolet radiation in the wave length from 2200 to 4000 Å. It can be seen that in the case of the G.E. UA-2 lamp shown here, as with all mercury vapor lamps, there are numerous band emissions present in the spectral distribution. If the total energy flux is matched over the region from 2200 to 4000 Å, this matching produces, at certain wave lengths, about a fivefold difference in flux compared to

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that of the sun. If the matching is done for the region between 2200 and 3000 Å a much closer simulation of the solar radiation is obtained. However, if the photochemical reaction of the coating is significantly dependent on wave length; that is, if it gives one product at one wave length and another kind of product at another wave length, or if synergistic effects occur through combination of wave lengths, it is very unlikely that satisfactory simulation with any lamp source of this kind is possible.

Experimental Polyvinyl Chloride Films for Developing Simulation Techniques

Thin films of pure polyvinyl chloride were cast from dilute solutions in methyl ethyl ketone. After being dried in air these were water-white transparent films. After further drying, at 60° C under vacuum, to remove traces of the ketone solvent the films were used in photodegradation studies. Similar films were prepared from a vinyl-chloride, vinyl-acetate, maleic-acid (86:13:1) terpolymer ("VMCH"). These films were cast from solutions containing toluene and methyl Cellosolve, and were dried in a similar manner. The VMCH terpolymer was also studied in combination with a metal substrate. Thin films were cast and affixed to aluminum disks by completing the removal of solvent at 80° C under vacuum. Film thicknesses were calculated to be 7 to 8×10^{-4} cm from the weight of film, density of polymer, and surface area. These films were used in the exposure tests to be described below.

Environmental Simulation Exposure Conditions

The films were irradiated for periods of time up to 72 hours with the total output of a G.E. UA-2 lamp (fig. 5) at a distance of 10-1/2 inches from the film surface. Under these conditions, the output of this lamp amounted to an average of one solar constant in the same wave-length region. The power output of the lamp was maintained constant during the entire exposure by monitoring the output with a photo cell and adjusting the input power as the lamp output degraded. During the radiations the vacuum chamber pressure was between 30 and 40 microns. The films were transferred to a vacuum dessicator where they were kept until spectroscopic measurements were made. The ultraviolet spectra were measured for the films before and after irradiation with a Cary 14 spectrophotometer. The infrared spectra of the films were obtained with a Perkin-Elmer 21 spectrophotometer. The change in reflectance of the terpolymer on the aluminum substrate was determined with a Gier Dunkel integrating sphere spectrophotometer.

The solar absorptance and emittance were determined by Lockheed Missiles and Space Company in a manner described in reference 1.

Discussion of Results

It was found convenient to present and consider the spectroscopic changes in films in terms of the optical density defined by the equation

$$O.D. = \ln I_0/I$$

where I_0 is the incident intensity and I is the transmitted intensity, a change in optical density $(\Delta(O.D.))$ of, say, 1.4, implies that the transmission, T $(=I/I_0)$, is essentially reduced to a level which is $10^{-1.4}$ or about 4 percent of the original transmission value. The method of representing the spectroscopic changes in the films by optical density rather than transmission or other quantities, was selected so that the changes in absorption could be related directly to the increased concentration of the color-producing groups. The changes in optical density of the free films of pure polyvinyl chloride with time of exposure to radiation in the wave-length region 2200 to 6000 Å are given in figure 6. The change in optical density, as plotted, is the difference in optical density (or absorption) of the polymer film at a given wave length before and after irradiation. The increase in the optical density and the shift of over-all absorption into the visible region is evident. After a total exposure of 6 hours, the polymer is nearly completely opaque to radiation at 2800 Å.

The basic chemistry underlying this photochemical change in PVC, based on references 3 and 5, is outlined in figure 7. The first step in this process is assumed to involve absorption of energy by trace impurities in the system in the form of unsaturated end groups, catalyst residue, residual solvent, etc. This energy absorption, followed by energy transfer to the basic polymer, is sufficient to initiate the reaction through the removal of an energetic chlorine atom, leaving a residual radical on the chain as shown. Propagation of the reaction involves the removal of the hydrogen atom immediately adjacent to the radical site to form a molecule of hydrogen chloride, termination occurs by formation of a π bond from the available pair of electrons. It has been shown by Boyer (ref. 6) that the continued introduction of double bonds by this mechanism is a nonrandom process, indicating that the removal of chlorine next to the double bond site proceeds more easily than the removal of chlorine from an ordinary carbon in the polymer chain. As the process proceeds, a conjugated linear polyene system is developed which absorbs strongly in the ultraviolet and visible region of the spectrum. To date, the exact concentration and extent of the conjugated system is unknown. Photochemical investigations are under way to determine the nature of this structure.

The change in optical density for pure PVC for a number of wave lengths from 2800 to 6000 Å as a function of time of ultraviolet radiation is shown in figure 8. This figure shows that there is increased opacity at all wave lengths over the ultraviolet and visible regions, and that the region of almost complete opacity (change in optical

density in excess of about 2.0), progressively advances to longer wave lengths with increased dose. No difference has been observed in the rate of color formation between the polyvinyl chloride and polyvinyl chloride terpolymers. In the cases of both polymers, no change in the infrared spectrum of the free films has been observed up to as much as 72 hours of ultraviolet radiation in vacuum.

As mentioned before, for the proposed flight tests, it is necessary to have a polymer which adheres well to an aluminum metal substrate, and is sufficiently flexible as well, so as to not crack during the expected temperature cycle (similar to fig. 1). The vinyl-acetate component of the VMCH terpolymer provides internal plasticization and the maleic acid provides the necessary polar groups for adhesion to the substrate. It is interesting to note that the ultraviolet-induced changes in optical density of this terpolymer are similar to those obtained for pure polyvinyl chloride.

In addition to ultraviolet radiation, the flight tested surfaces experience collisions with higher energy photons in space. For this reason, the effects of gamma radiation from 10 to 16 mev were also examined on the polyvinyl chloride films. Figure 9 shows the changes in optical density produced by ν radiation. An essentially analogous situation is obtained here in the way in which the opacity at each wave length steadily increases with increased gamma radiation. An increase in optical density with increasing dose similar to that for ultraviolet radiation is observed. The near equivalence of the effects of ultraviolet radiation and gamma radiation is shown in figure 10. It is clear that a dose of 9 hours of solar ultraviolet energy produces a change equivalent to a dose of gamma radiation of 10 megarads. It would probably take a period of at least 3 to 4 years to obtain a dose of this magnitude from the higher energy photons available in the environment of the OSO satellite, whereas, a similar effect would be produced in a few hours of ultraviolet radiation. These results indicate that the effects of higher energy photons in space can be ignored in this ultraviolet degradation comparison.

The temperature rise which occurred during exposure of the VMCH film on aluminum substrate to ultraviolet radiation in vacuum is given in figure 11. It can be seen that there is a rise in temperature from 27° C to about 46° C in 1200 minutes. Since no change in the rate of formation of chromophore was observed in these tests it appears that the activation energy for the dehydrochlorination of polyvinyl chloride is very small under these conditions. No precautions were taken to control or to correct for the energy emitted from the back face of these composites or to shield this surface, therefore, this temperature rise does not quantitatively indicate the expected temperature rise on the satellite experiment.

The decrease in the percent of energy reflected due to 16.5 hours of irradiation with the UA-2 lamp of the VMCH terpolymer cast on an aluminum substrate is given in figure 12. The percent reflectance as

a function of wave length from 3000 to 28,000 Å was determined by the Gier Dunkel hemispherical reflectance spectrophotometer. The shaded area indicates the wave-length region of change in reflectance due to alteration in the film properties. It can be seen that the largest change in reflectance occurs in the visible and ultraviolet region below 7000 Å. This corresponds to the region of change in optical density for the free films of this polymer, and suggests that on the aluminum substrate, the production of chromophores in the polymer is still the principal cause of change in optical properties. It can be seen that above 9000 Å, there is little change in the absorption with ultraviolet exposure, a result also anticipated from infrared absorption spectra of the free films. This behavior of the reflectance spectra indicates that a relatively constant value of emittance and a rapid change of the solar absorptance of this system with time of ultraviolet irradiation can be expected. The initial value of solar absorptance of 0.23 changes to 0.45 with 16 hours of irradiation while the emittance remains constant at a value of 0.60.

The change in the ratio of solar absorptance to emittance for the VMCH terpolymer on aluminum substrate after irradiation at one solar constant between 2000 and 2700 Å for exposure times up to 1500 minutes is given in figure 13. It can be seen that after an initial relatively rapid rise, the change in the ratio of solar absorptance to emittance continues to rise linearly. The change in α/ϵ over the test period is significantly large. The temperature changes calculated for these increases in ratio of solar absorptance to emittance as a function of exposure time are given in figure 14. These results indicate that a temperature increase of 35° C over a test period of 1500 minutes can be expected.

CONCLUDING REMARKS

These results indicate that polymers of vinyl chloride may be satisfactory comparators for correlating the changes in solar absorptance produced by exposure to ultraviolet radiation in flight and ground-based tests. These polymeric films meet the criteria for a well-behaved system, in that they undergo a regular change in optical density with time of exposure, and the change in solar absorptance can be measured easily as a change in temperature. Furthermore, the photochemistry occurring in vacuum is free from complicating side effects such as surface erosion and depolymerization characteristic of many polymers.

Because of the extreme sensitivity of the ultraviolet and visible absorption spectra to the chromophore concentration, these films may find application as accurate ultraviolet dosimeters if it can be shown that the quantum efficiency for the production of these color-forming groups is independent of the wave length of absorbed photons in the photochemically productive region.

These films will be flown on the S-57 OSO satellite sometime in 1964, at which time it will be possible to compare the temperature changes predicted by laboratory tests with in-flight measurements directly.

Future plans include improvements in matching the photochemically productive region of the solar spectrum in the laboratory tests and a critical analysis of the kinetics of the chromophore reaction.

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FIGURE LEGENDS

Figure 1.- Observed variation in surface temperatures of TiO_2 epoxy and TiO_2 silicone in a single orbit of S-16 OSO satellite.

Figure 2.- Changes in solar absorptance of TiO_2-epoxy and TiO_2-silicone coatings due to environmental aging.

Figure 3.- A comparison of predicted increase in solar absorptance of TiO_2-epoxy coating with in-flight results on S-16.

Figure 4.- A comparison of predicted increase in solar absorptance of TiO_2-silicone coating with in-flight results on S-16.

Figure 5.- Comparison of the spectral distribution of G.E. UA-2 lamp and solar spectrum in ultraviolet and near infrared regions.

Figure 6.- Change in optical density of polyvinyl chloride in the ultraviolet and visible region with time of exposure to G.E. UA-2 lamp in vacuum.

Figure 7.- Radiation production of chromophores in polyvinyl chloride.

Figure 8.- Change in optical density at various wave lengths of polyvinyl chloride from 2800 to 6000 Å as a function of time of exposure to a G.E. UA-2 lamp.

Figure 9.- Change in optical density of polyvinyl chloride at various wave lengths as a function of γ irradiation dose.

Figure 10.- Equivalency of ultraviolet irradiation dose to gamma dose for polyvinyl chloride.

Figure 11.- Change in surface temperature of polyvinyl chloride (VMCH) copolymer on aluminum substrate dueing irradiation in vacuum at a constant flux with G.E. UA-2 lamp.

Figure 12.- Change in reflectance of polyvinyl chloride copolymer (VMCH) on aluminum substrate due to irradiation in vacuum with G.E. UA-2 lamp.

Figure 13.- Increase in ratio of solar absorptance to emittance for polyvinyl chloride copolymer (VMCH) on aluminum substrate due to exposure to G.E. UA-2 lamp.

Figure 14.- Predicted temperature change in polyvinyl chloride copolymer (VMCH) on aluminum substrate as a function of exposure time.
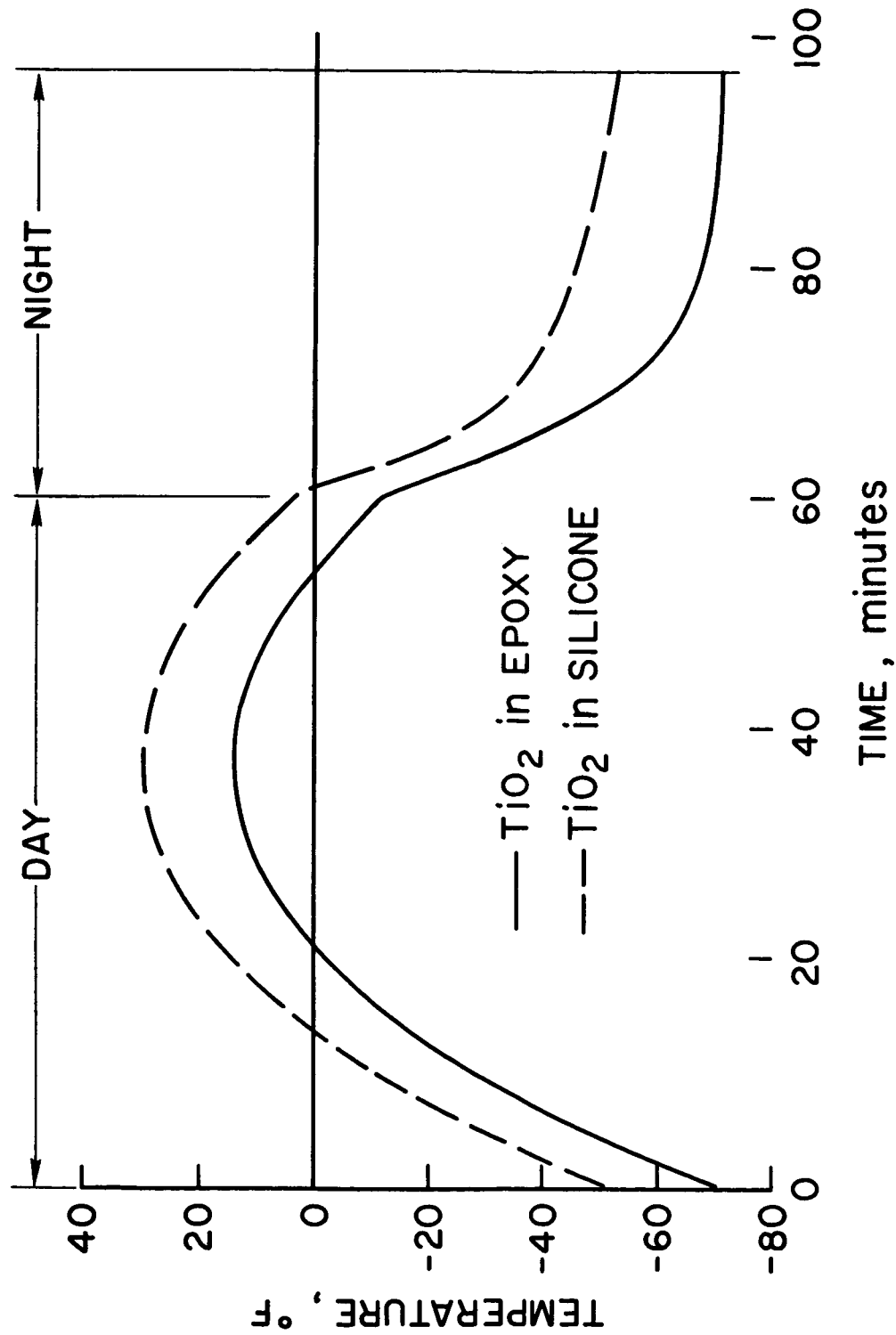
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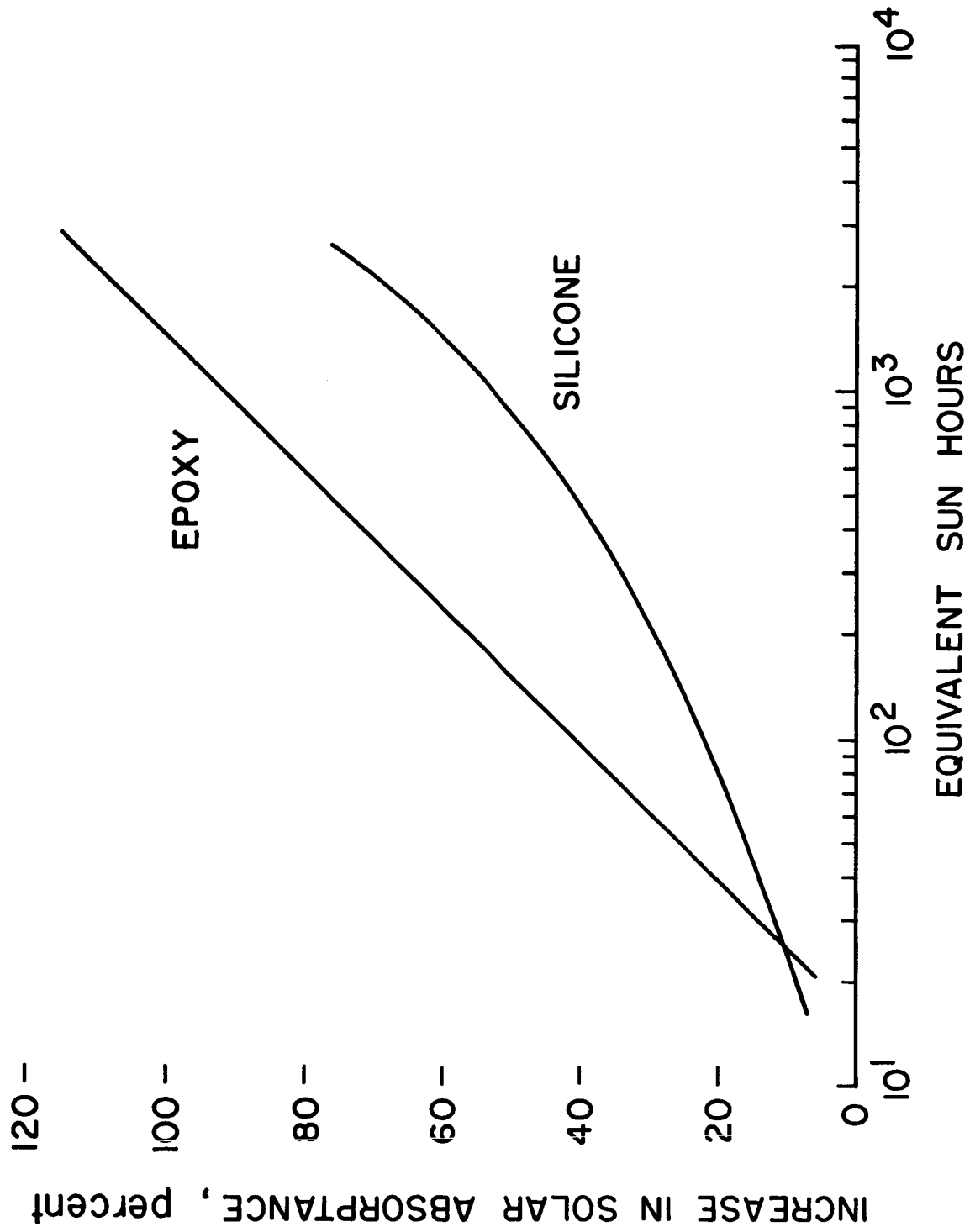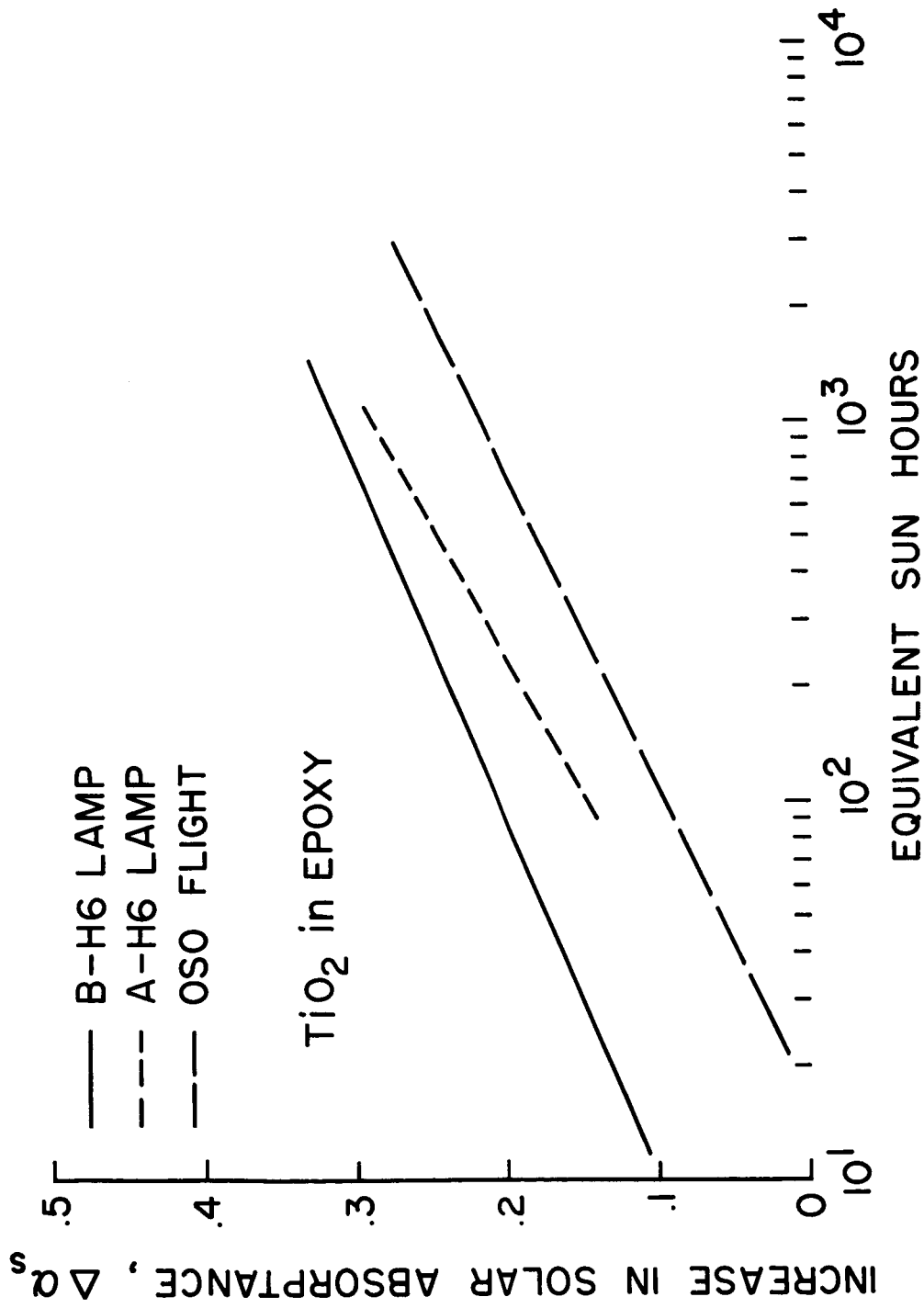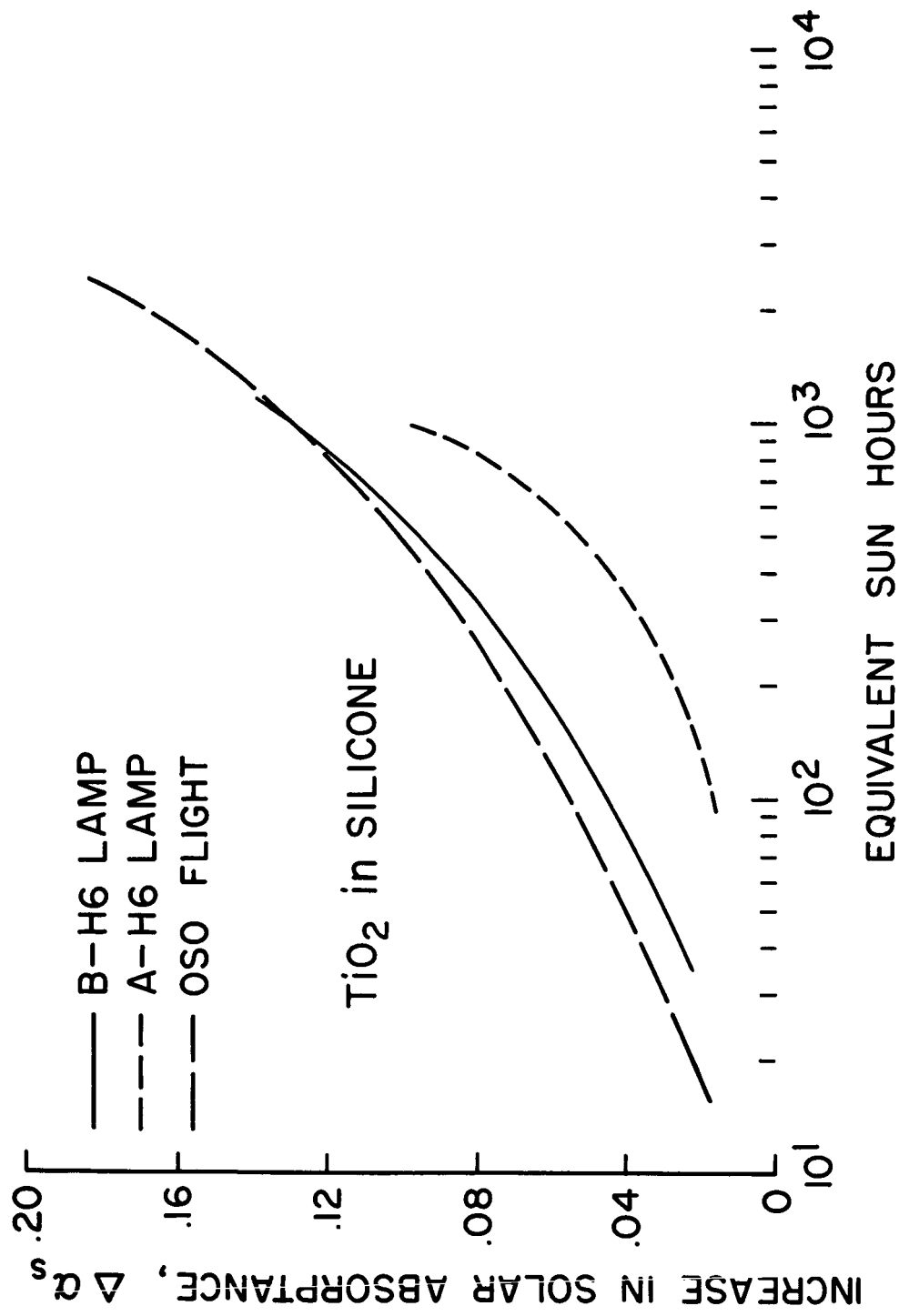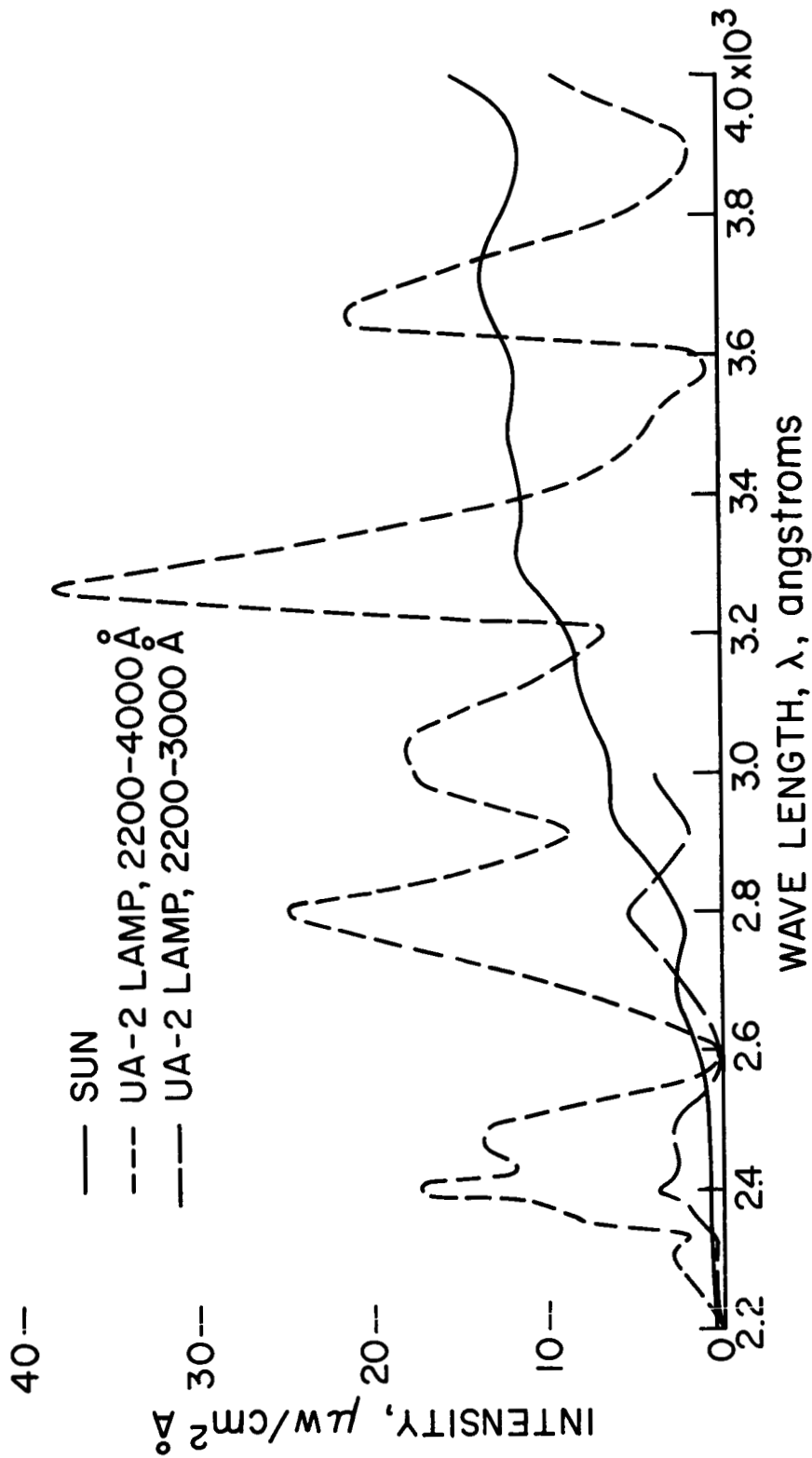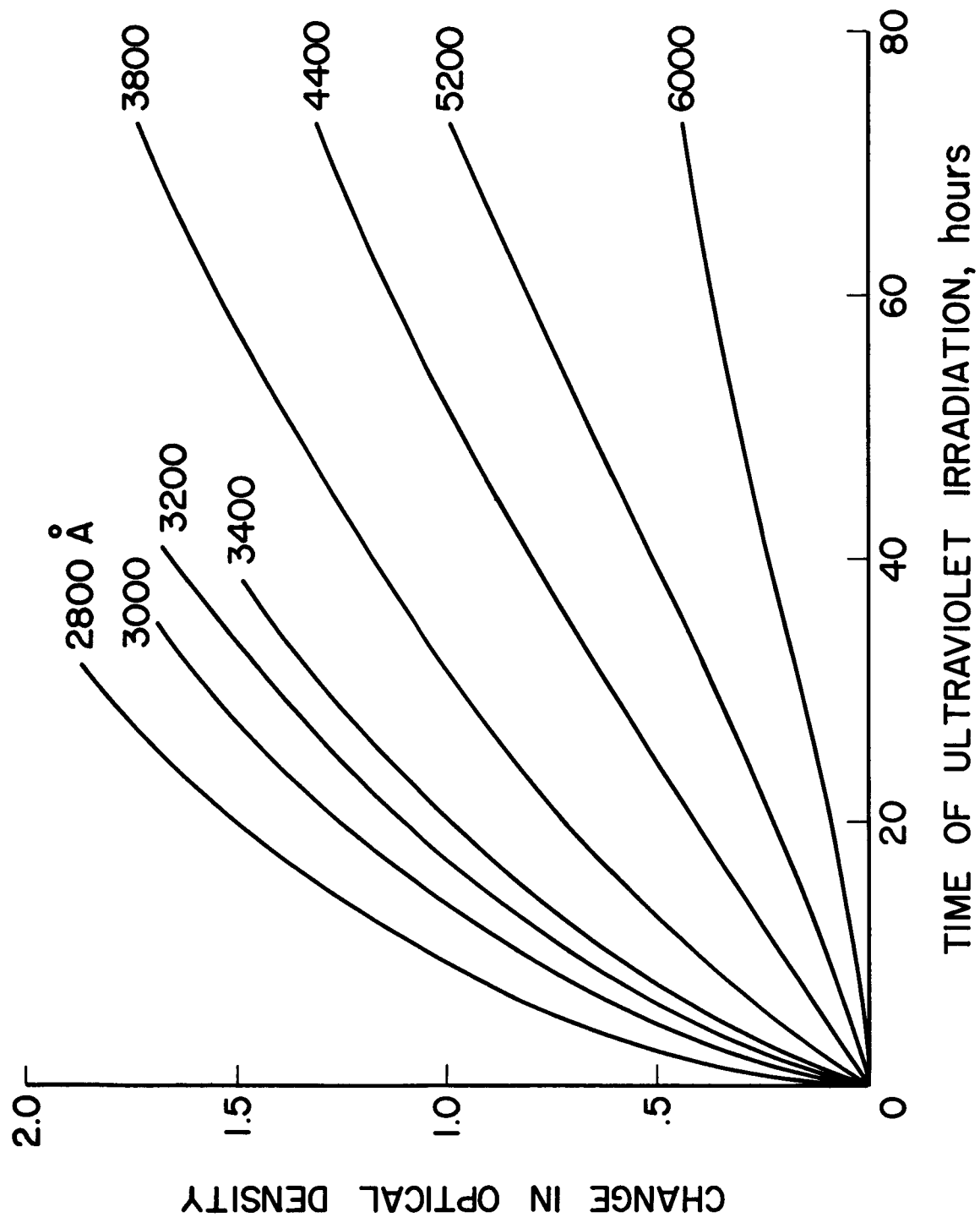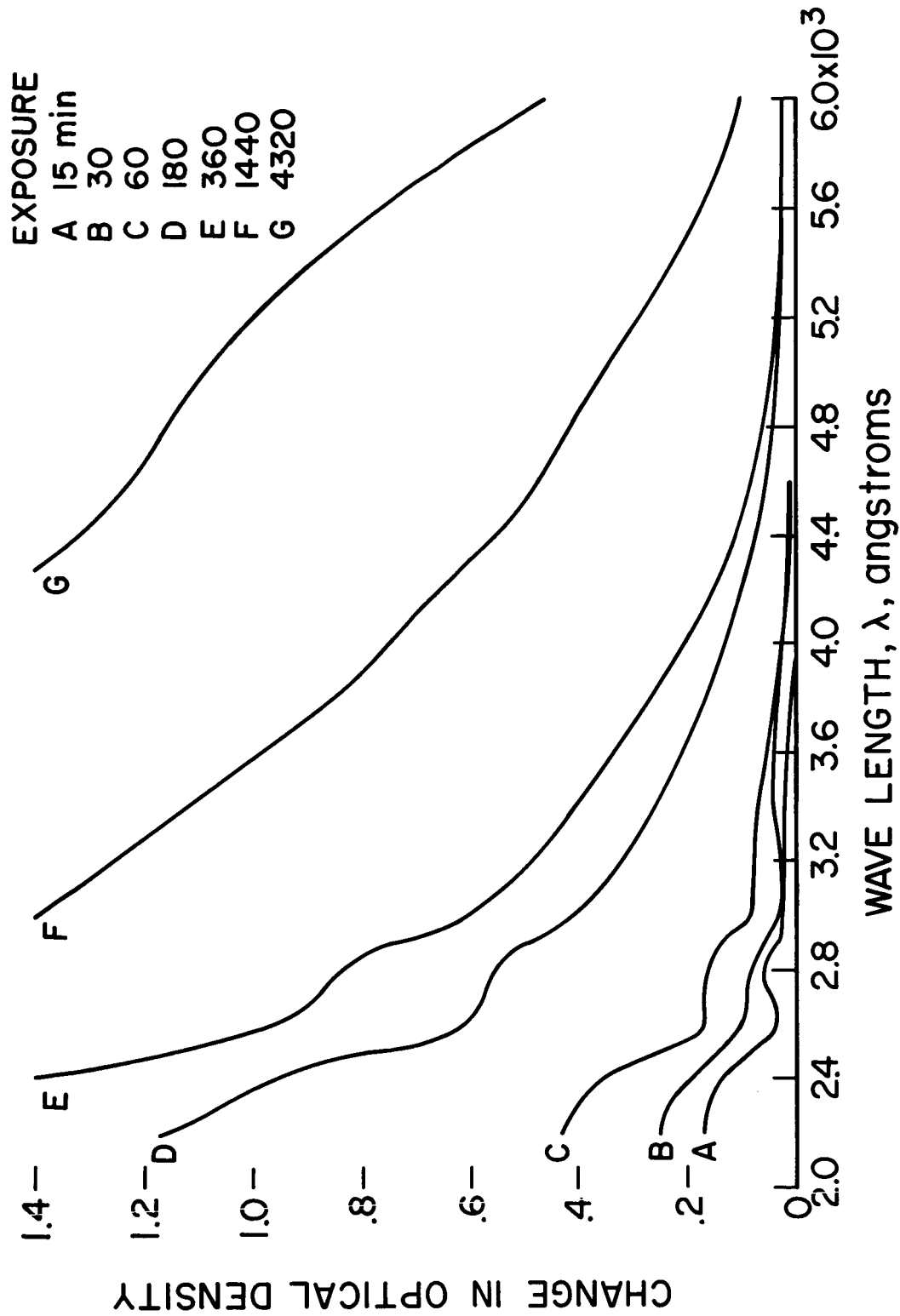
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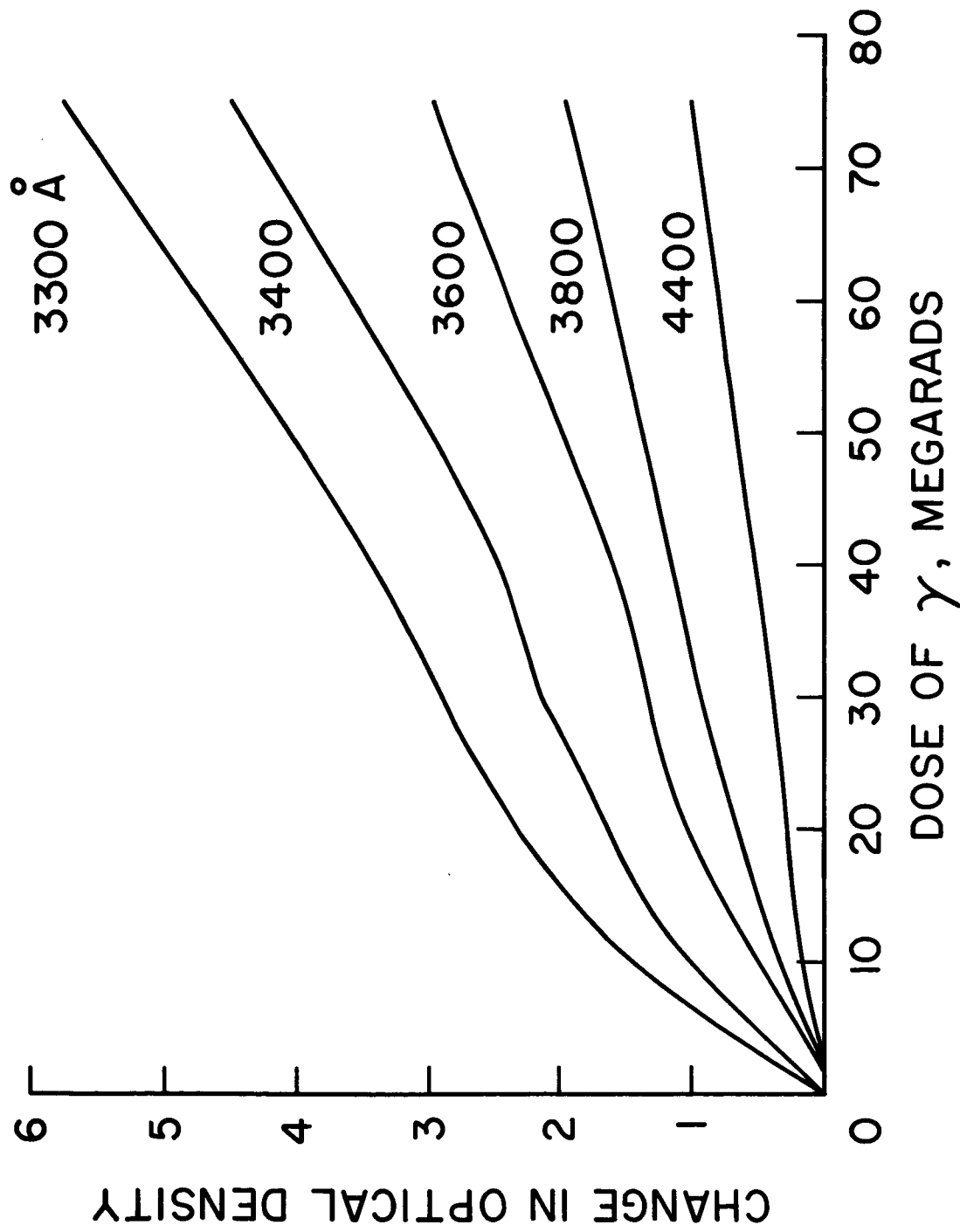
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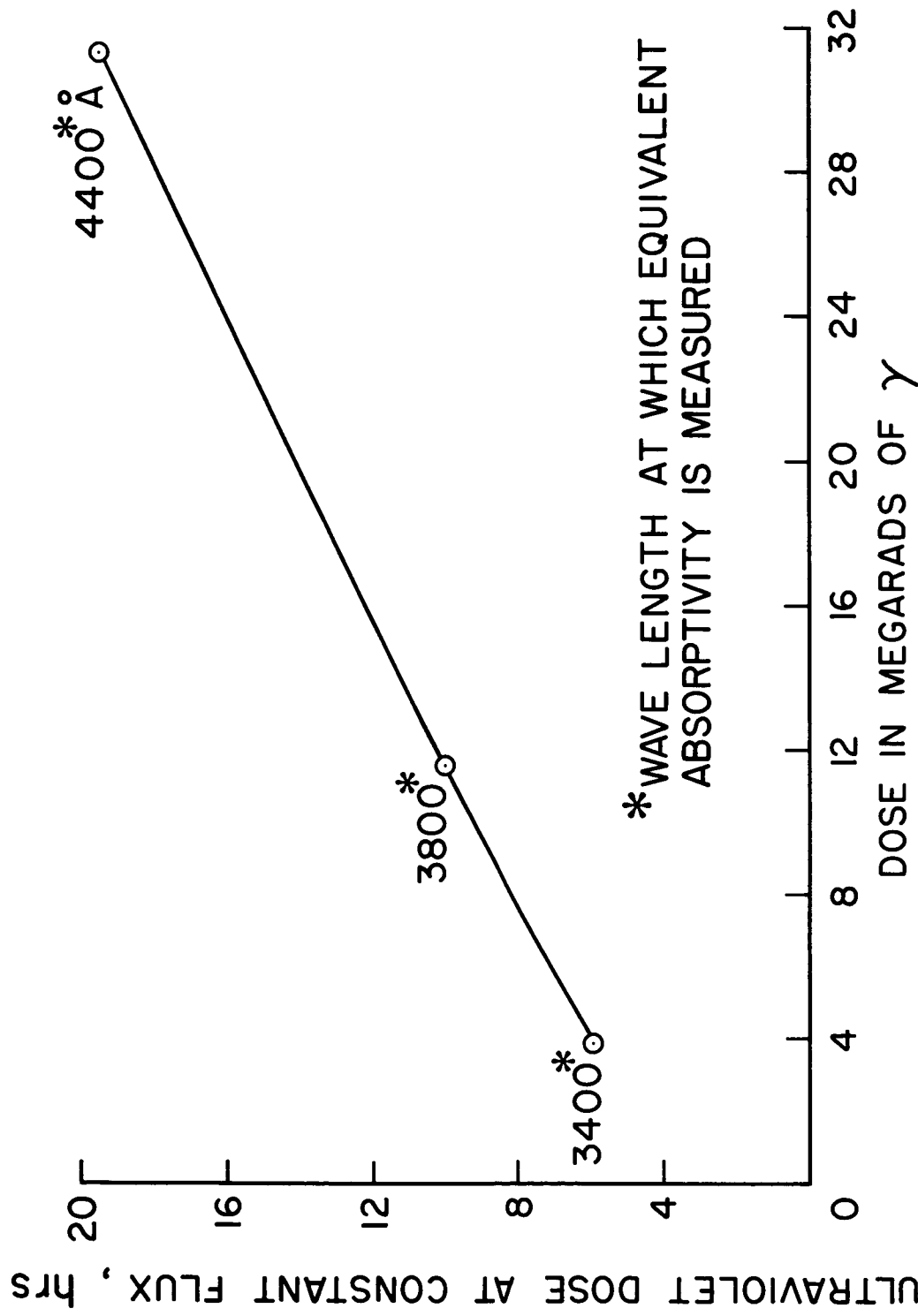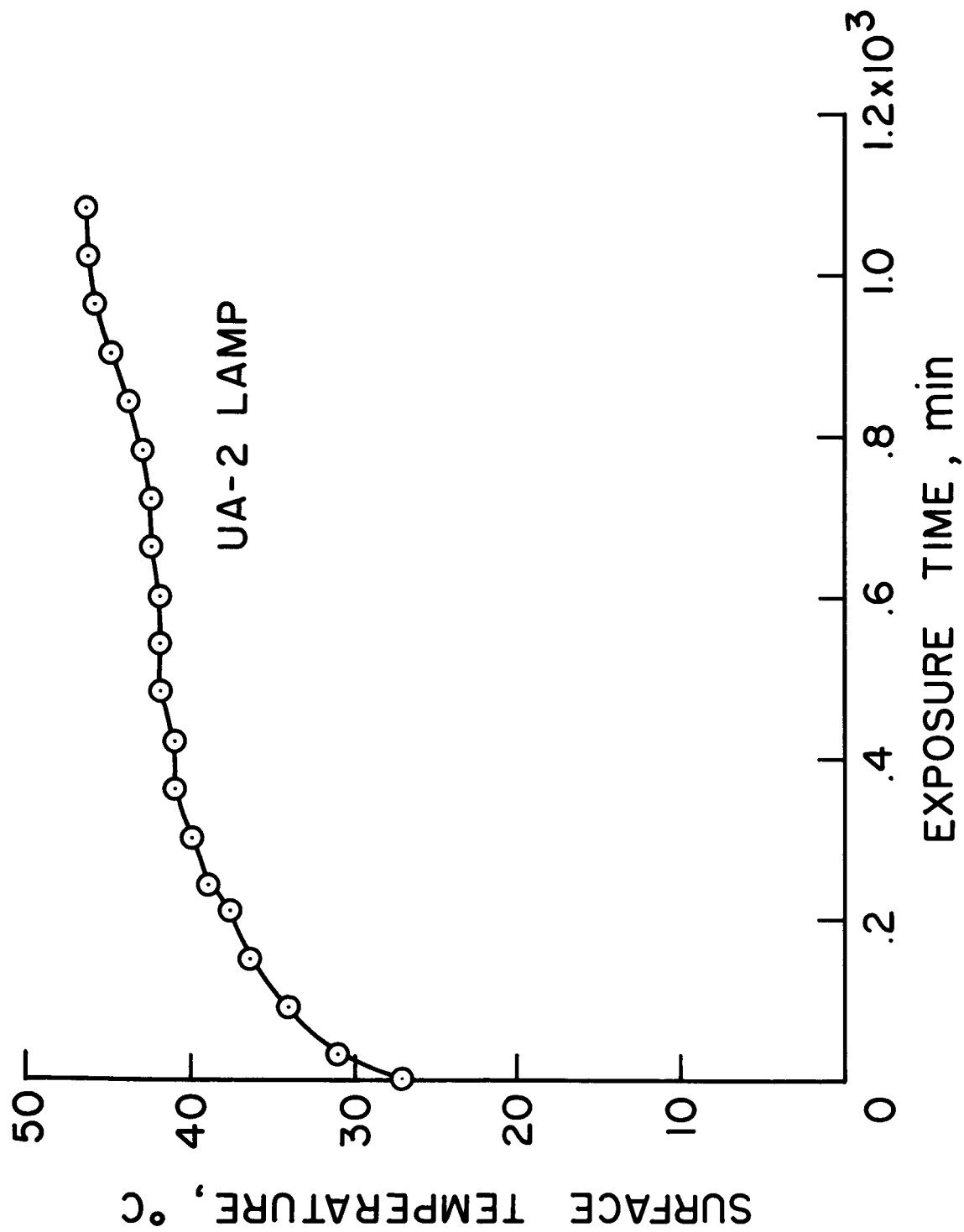
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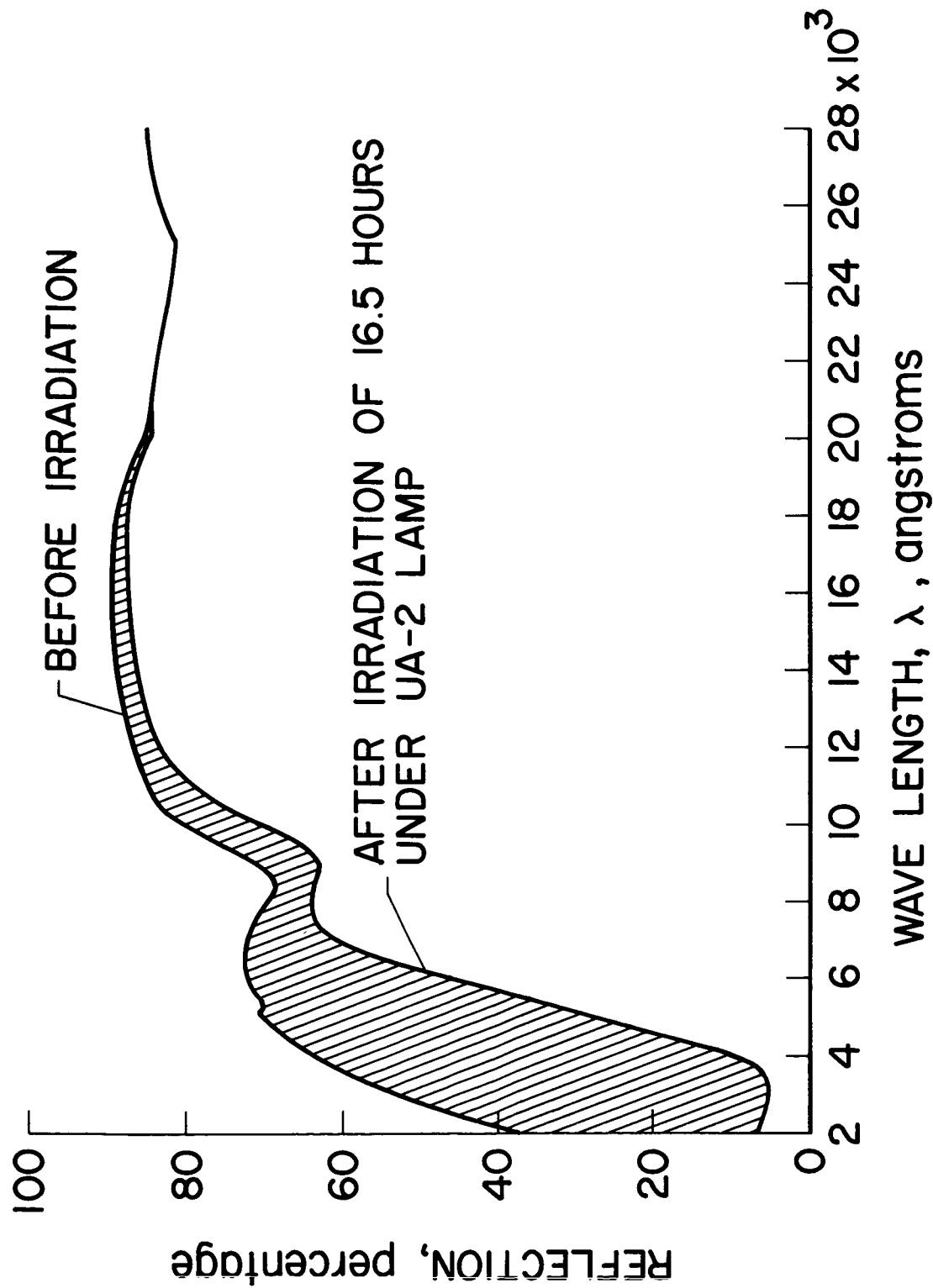
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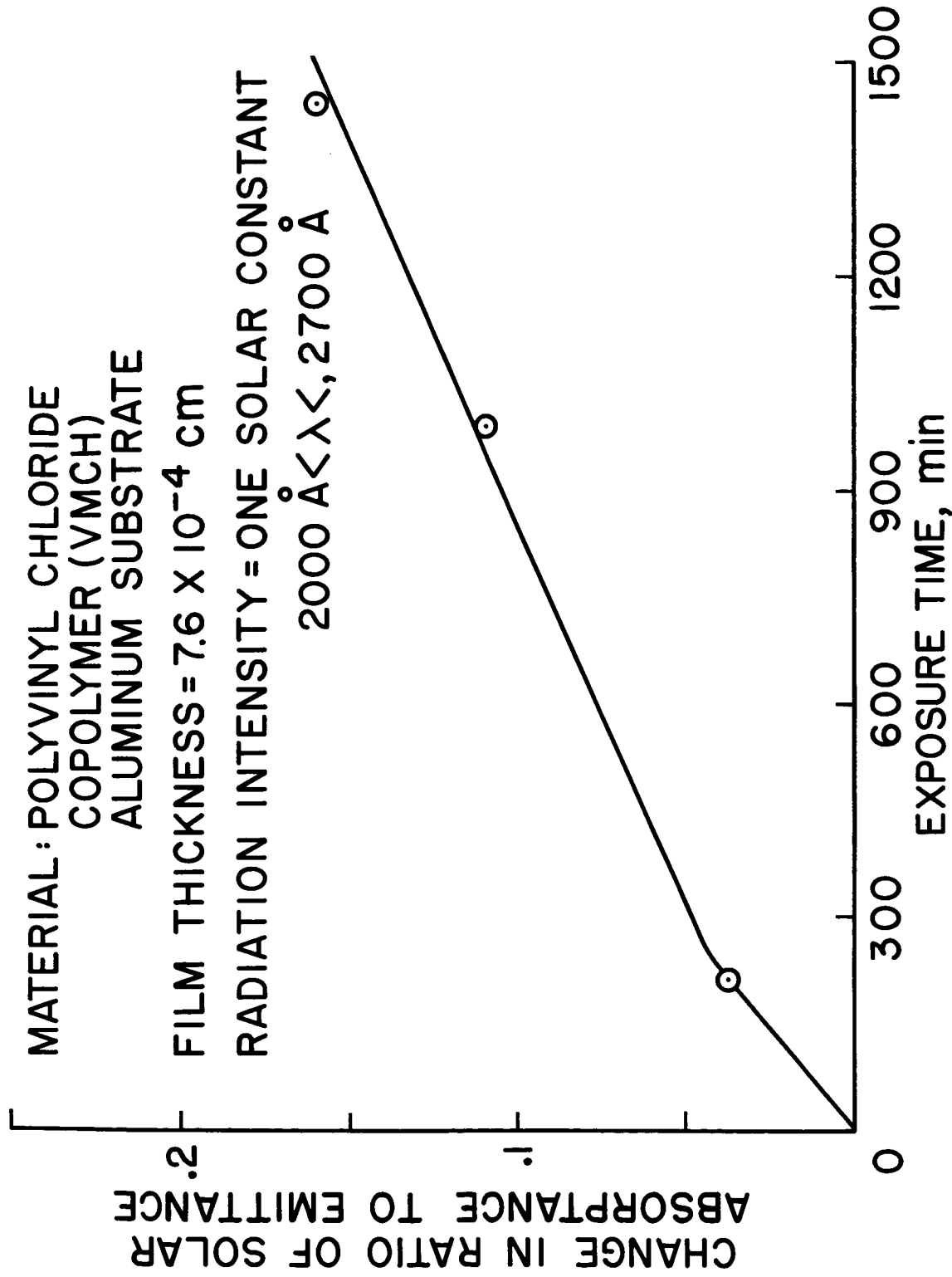
Figure 13.- Increase in ratio of solar absorptance to emittance for polyvinyl chloride copolymer (VMCH) on aluminum substrate due to exposure to G.E. UA-2 lamp.
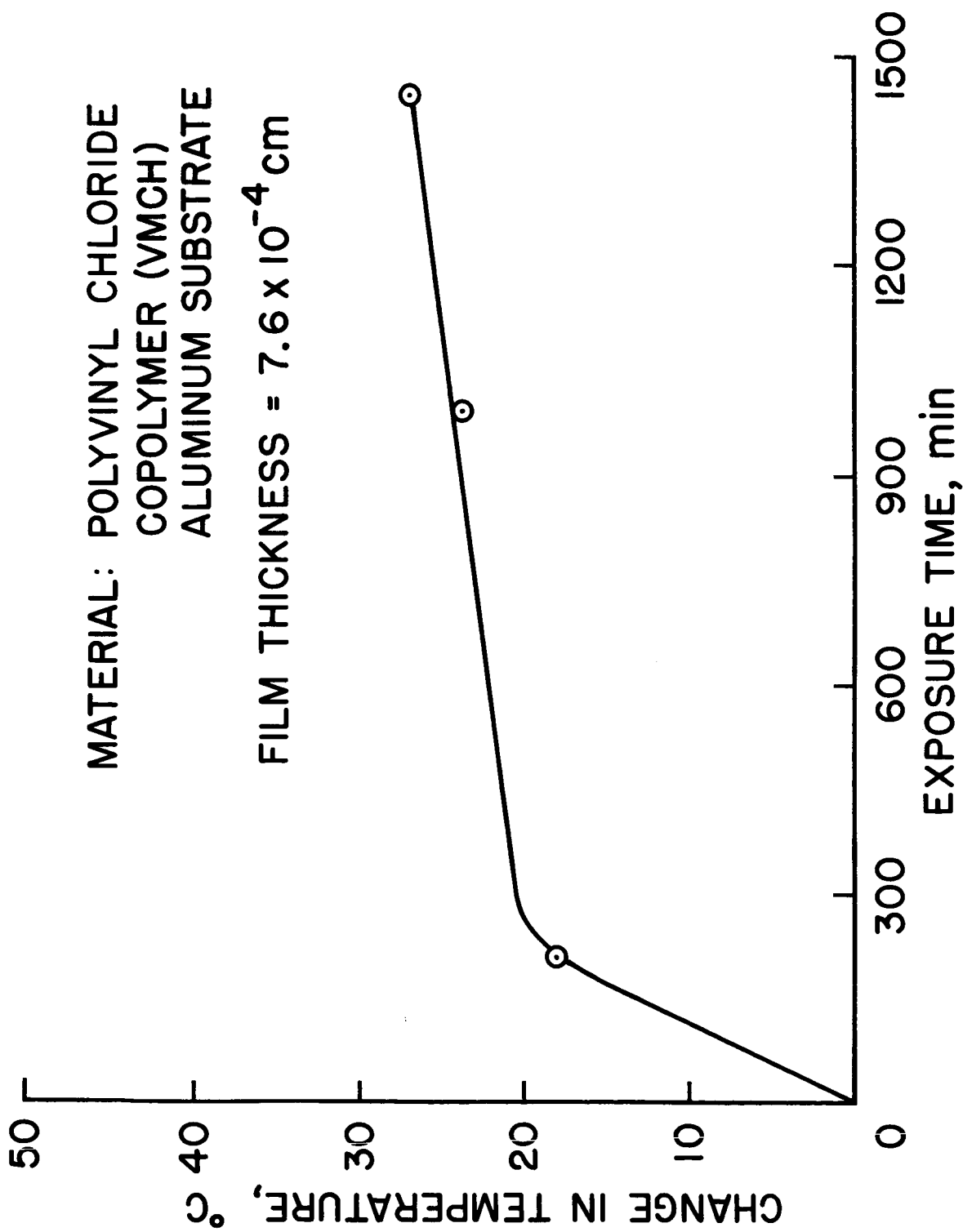
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